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Growing of thallium-doped KDP and ADP crystals: structural and optical parameters

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Studied has been the influence of thallium activator on the growth kinetics and structure perfection of KDP and ADP crystals, the character of its incorporation and distribution in the crystal lattice and the photoluminescence properties. Revealed has been thallium incorporation anisotropy in the prism and pyramid growth sectors of ADP crystals which may be caused by the charge state of the {100} and {101} growth planes. For KDP crystals, thallium incorporation is limited by the ionic radii difference of the K^+ and Tl^+ cations. Doping with thallium in amounts up to 1.0 mass % causes no changes in the structure perfection of KDP and ADP crystals. Thereat, for ADP crystals, there the increase of the lattice parameter a by $0.9 \cdot 10^{-3} \pm 3 \cdot 10^{-5}$ Å is revealed and the decrease of the parameter c by $1.1 \cdot 10^{-3} \pm 3 \cdot 10^{-5}$ Å. The thallium absorption band in KDP:Tl^+ and ADP:Tl^+ crystals lies near 220 nm, emission band maximum is at 280 nm.

Изучено влияние активатора таллия на кинетику роста и структурное совершенство кристаллов KDP и ADP, характер вхождения и распределение его в кристаллической решётке и на фотолюминесцентные свойства. Обнаружена анизотропия вхождения примеси таллия в секторы роста призмы и пирамиды кристаллов ADP, что может быть обусловлено зарядовым состоянием плоскостей роста {100} и {101}. В кристаллах KDP вхождение примеси таллия лимитируется различием ионных радиусов катионов K^+ и Tl^+. При легировании таллием до 1.0 масс.% кристаллов KDP и ADP изменения структурного совершенства не установлено. При этом обнаружено увеличение параметра решётки a на $0{,}9 \cdot 10^{-3} \pm 3 \cdot 10^{-5}$ Å и уменьшение параметра c на $1{,}1 \cdot 10^{-3} \pm 3 \cdot 10^{-5}$ Å для ADP кристаллов. Полоса поглощения таллия в кристаллах KDP:Tl^+ и ADP:Tl^+ лежит в области 220 нм, максимум полосы эмиссии приходится на 280 нм.

KDP (KH_2PO_4) and ADP ($NH_4H_2PO_4$) single crystals are well-known non-linear optical crystals with a wide optical transparency band of 175 to 1500 nm [1, 2]. These crystals possess a high radiation resistance: their absorption coefficient remains unchanged under irradiation at doses up to 10^{13} cm^{-2} for protons, 10^{10} cm^{-2} for neutrons and 10^5 rad for γ-particles [3]. As is known [4], inorganic alkali halide crystals containing ammonium group and doped with thallium can be used to detect neutrons with energies of 1.0 MeV and higher. KDP and ADP crystals with different activators introduced into the crystal lattice (e.g. thallium) also can be applied for neutron detection. Neutrons are registered using recoil protons in the elastic scattering process of neutrons on hydrogen atoms.

In this work, the growing conditions were studied for thallium-doped KDP:Tl^+ and ADP:Tl^+ crystals from aqueous solutions of stoichiometric composition (pH = 4.0 for KDP and pH = 3.2 for ADP). As the starting material, we used potassium and ammonium dihydrophosphate salts with total content of microimpurities not higher than $1 \cdot 10^4$ mass %. The activator concentration in the initial solution was 0.01; 0.1; 1.0 mass %. The microimpurities and thallium in the initial solutions and in the grown crystals was determined using standard chemical and spectral

Table 1. Growth conditions for thallium-doped KDP and ADP crystals

Tl, % mass. (solution)	Tl, % mass (prism)		Tl, % mass (pyramid)		V_z mm/24 h		$V_{x,y}$ mm/24 h	
	KDP	ADP	KDP	ADP	KDP	ADP	KDP	ADP
0.01	$0.83 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$0.94 \cdot 10^{-3}$	$0.56 \cdot 10^{-2}$	5.83	4.0	6.58	3.0
0.1	$0.88 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$	$0.73 \cdot 10^{-2}$	$0.54 \cdot 10^{-1}$	6.0	3.75	5.6	3.0
1.0	$1.2 \cdot 10^{-1}$	0.69	$1.0 \cdot 10^{-1}$	0.44	5.75	3.75	2.62	3.3

analysis methods. The crystals were grown on point seed by high-rate method with temperature decrease in the 50–30°C interval. The seed planes were oriented with respect to the (100), (010), (001) crystallographic planes to within 30′. The growth rate was 4–7 mm/24 h. It was determined as the averaged value of the grown crystal size ratio to the growth time. The structure parameters of the grown crystals were established using the precision three-crystal X-ray diffractometry in monochromic CuK_α radiation. The degree of the measurement accuracy was attained by formation of primary X-ray beam with a low angular and spectral divergence which allowed to obtain the diffraction reflection curves (DRC) with the half-width β of 7 to 10″. This permitted to minimize errors while reproducing the DRC shape and half-width (β) and the X-ray beam reflection integral coefficient value I^R_{exp} down to 2 %, to enhance the determination accuracy of the crystal lattice parameter $\Delta d/d$ up to $2 \cdot 10^{-7}$, as well as to use β, I^R_{exp}, $\Delta d/d$ as a measure of structure perfection for the grown crystals [4]. Optical and spectral investigations of KDP:Tl^+ and ADP:Tl^+ crystals were realized using a SF-56 spectrophotometer and an "Eclipse" spectrofluorimeter produced by Varian. The optical absorption and photoluminescence spectra were measured in the 200–600 nm range.

The thallium impurity has been established to influence the growth conditions of the {100} prism sectors and the {101} pyramid ones of KDP and ADP crystals in essentially different fashions. In particular, in the case of KDP:Tl^+, the growth rates of the prism faces in the directions X [100] and Y [010] are not the same and reduce as the thallium concentration in the solution increases. At the same time, the growth rate of the pyramid faces in the direction Z [001] is independent of thallium concentration in the solution. Table 1 presents the data on the influence of the thallium content in the solution on the crystal growth rate and the chemical analysis results of thallium incorporation into the crystal lattice. The growth rate difference for the prism and pyramid faces results in changes in the crystal's habitus. As the thallium concentration in the solution increases, the growth of the prism faces is suppressed and the crystal becomes extended along the Z [001] direction, the crystal cross-section shape in the Z (001) plane is different from quadratic and tends to rectangular one. As to ADP:Tl^+ crystals, the increase of thallium content in the solution does not result in such noticeable changes in the growth rate of the prism faces and in the crystal habitus.

The results of chemical analysis clearly show an essential distinction in the character of thallium incorporation into the KDP and ADP crystal lattices. In KDP:Tl^+ crystals, this impurity is distributed over the prism and pyramid growth sectors relatively homogeneously. The incorporation coefficient of the doping impurity into the said growth sectors of KDP crystals is about 0.1. In ADP:Tl^+ crystals, the thallium content in the prism sectors is twice as high as that in the pyramid sectors, and this corresponds to the thallium incorporation coefficients into the prism and pyramid sectors of 1.0 and 0.5, respectively.

Measurements of the crystal lattice parameters a and c depending on the impurity concentration show that in KDP:Tl^+ crystals, the parameter a increases by $\Delta a = 1.5 \cdot 10^{-4}$ Å and the parameter c decreases by $\Delta c = 1.5 \cdot 10^{-4}$ Å as the mentioned concentration risesup to 0.1 mass %. For ADP:Tl^+ crystals, the content of thallium attains 1.0 mass %, the parameter a increases in this case by $\Delta a = 9 \cdot 10^{-4}$ Å and the parameter c diminishes by $\Delta c = 11.2 \cdot 10^{-4}$ Å. The dependences of the lattice constants a and c on the thallium concentration in the crystal are shown in Fig. 1 for KDP:Tl^+ and in Fig. 2 for ADP:Tl^+. The measured values of the crystal lattice parameters correlate with the chemical analysis data: incorporation of thallium impurity into the prism sector of

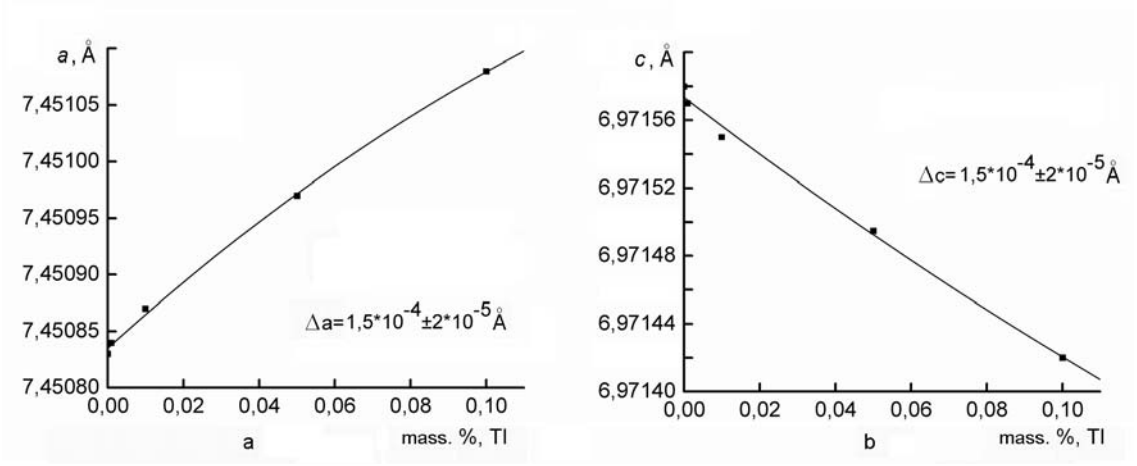

Fig. 1. Dependence of the lattice periods *a* (*1*) and *c* (*2*) of KDP:Tl^+ crystal on the thallium concentration.

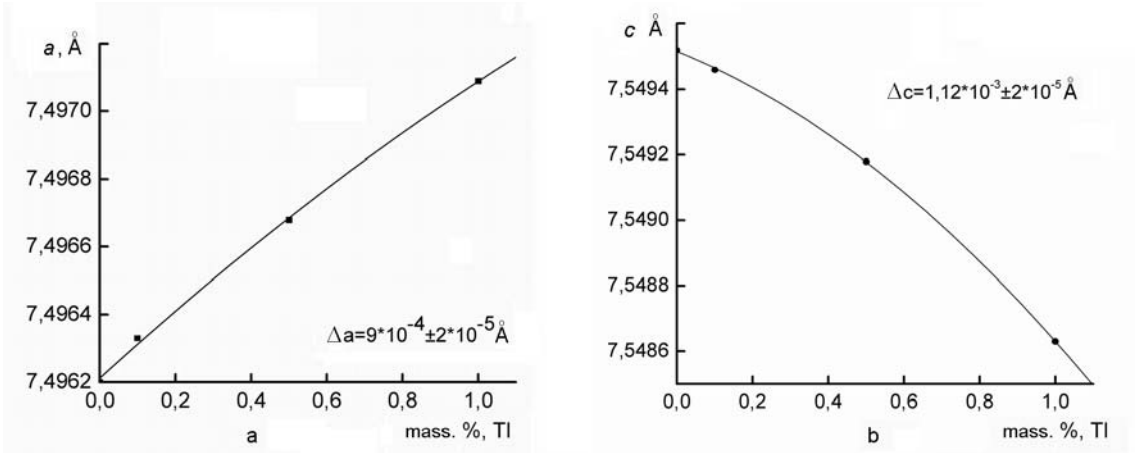

Fig. 2. Dependence of the lattice periods *a* (*1*) and *c* (*2*) of ADP:Tl^+ crystal on the thallium concentration.

KDP:Tl^+ is a decimal order lower than that in the case of ADP:Tl^+, and this is clearly seen as the difference in the parameter *a* change.

The thallium incorporation and distribution character in the KDP and ADP crystal lattices is defined most probably by the difference in the ionic radius values of K^+ (1.33 Å), NH_4^+ (1.45 Å) cations which form the lattice and of the impurity Tl^+(1.48 Å), as well as by the charge states of the growth planes in the prism {100} and the pyramid {101} [5, 6]. In the course of growth, the prism plane {100} is formed by phosphate-potassium packets and has no electric charge. The pyramid plane {101} is formed in turns by the tetrahedrons ($H_2PO_4^-$) and K cations, thus, acquires alternating negative and positive charges. The neutral plane {100} is constantly open for interaction with the cationic impurity, whereas the plane {101} interacts with that impurity only being charged negatively. A considerable distinction between K^+ and Tl^+ ionic radii (≥10 %) results in a small value of the thallium incorporation coefficient into the KDP crystal lattice (0.1) as well as in the fact that the impurity will be most probably located not only in the crystal lattice sites, but also in the interstitial space. In ADP:Tl^+, the distinction between the NH_4^+ and Tl^+ ionic radii is essentially smaller (≤2 %); thallium substitutes the ammonium group subject to the charged state of the growth planes, which results in the fact that the coefficients of thallium incorporation into the prism and pyramid are different (1.0 and 0.5, respectively).

As stated while comparing the rocking curves obtained for pure KDP and ADP crystals and for those doped with thallium (up to 0.1 mass % and 1.0 mass %, respectively), such a doping does not cause any deterioration of the structure perfection.

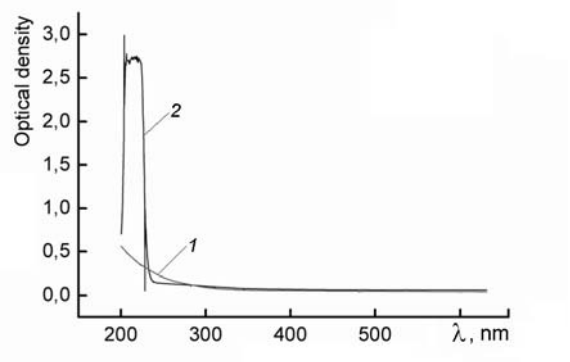

Fig. 3. Absorption spectra of nominally pure ADP (*1*) and ADP:Tl^+ (0.1 mass %) (*2*) crystals.

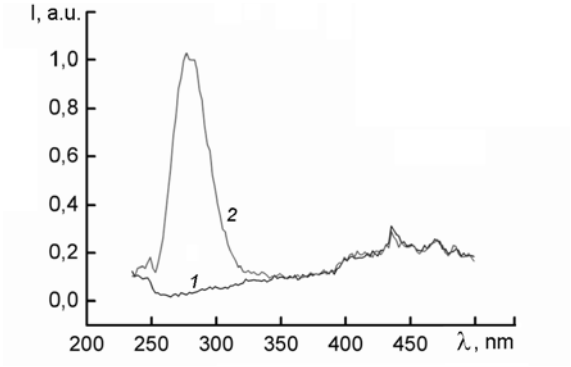

Fig. 4. Photoluminescence spectra of nominally pure ADP (*1*) and ADP:Tl^+ (0.1 mass %) (*2*) crystals.

The half-widths of the rocking curves lie within the interval $\beta = 7–10''$ for all the studied thallium concentrations. No essential changes are stated for the integral reflection power I^R_{exp} either, and this points to the fact that the density of two-dimensional defects in the crystal lattice is insignificant. Scanning of the sample by X-ray beam testifies that the structure perfection of the grown crystals is homogeneous over the cross-section. The measured structure-sensitive parameters of KDP:Tl^+ and ADP:Tl^+ crystals are presented in Table 2.

Optical spectra of the doped crystals show that in ADP:Tl^+, the thallium absorption band lies at about 220 nm. The absorption spectrum of the crystal with 0.1 mass % thallium concentration is presented in Fig. 3. The same Figure also contains the absorption spectrum of undoped ADP crystal which points to the absence of the absorption band associated with the doping impurity. Fig. 4 presents the photoluminescence spectra with the emission band maximum at 280 nm obtained under excitation of ADP:Tl^+ crystal with UV radiation of 220 nm wavelength. In the undoped crystals, no photoluminescence is observed. As to KDP:Tl^+ crystals, the excitation band maximum is shifted towards longer wavelengths (from 220 to 240 nm), as the thallium concentration rises, while the position of the photoluminescence emission band maximum remains unchanged, but the emission intensity increases. Fig. 5 presents the excitation and emission spectra for KDP:Tl^+ crystals with thallium concentration of 0.001; 0.01; 0.1 mass %. In the undoped crystals, photoluminescence is not observed either.

Comparison of the results obtained in this work concerning photoluminescence of thallium-doped KDP and ADP crystals with literature data [7–10] shows that the characteristic emission bands caused by the intrinsic defects (A- and B-radicals) in the 620–350 nm region of are absent at room temperature. The photoluminescence excita-

Table 2. Structure parameters of KDP and ADP crystals depending on the thallium concentration

	Tl^+, mass. %		Reflex	V, Å^3		β, arcsec		I·10^{-6}		d, Å	
	KDP	ADP		KDP	ADP	KDP	ADP	KDP	ADP	KDP	ADP
1	pure	pure	{800}	387.026	446.707	7.1	6.8	4.72	2.96	0.931354	0.937025
			{008}			7.4	6.6	8.4	5.43	0.871877	0.993690
2	$1\cdot10^3$	—	{800}	387.027	—	7.5	—	4.78	—	0.931355	—
			{008}			8.5	—	8.41	—	0.871446	—
3	$1\cdot10^2$	$1\cdot10^{-2}$	{800}	387.029	446.719	8	7	4.39	3.3	0.931359	0.937041
			{008}			9	6.9	9.16	5.3	0.871444	0.993683
4	$5\cdot10^{-2}$	—	{800}	387.039	—	7.8	—	4.82	—	0.931386	—
			{008}			9.2	—	9.2	—	0.871427	—
5	$1\cdot10^{-1}$	$1\cdot10^{-1}$	{800}	387.044	447.746	7.8	8.1	4.4	3.5	0.932465	0.937085
			{008}			9.3	7	9.3	5.2	0.871437	0.993648
6	—	$7\cdot10^{-1}$	{800}	—	446.764	—	7.3	—	3.35	—	0.937136
			{008}			—	7.6	—	6.66	—	0.993579

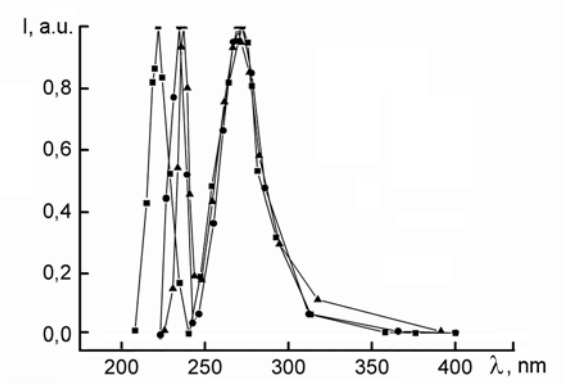

Fig. 5. Normalized excitation and photoluminescence spectra of KDP:Tl^+ crystals. Dopant concentration (per cent mass): 0.001 (squares), 0.01 (circles), 0.1 (triangles).

tion band of KDP:Tl^+ and ADP:Tl^+ crystals corresponds to the band of thallium impurity absorption in the crystals. The 280 nm absorption band may be attributed to intracenter activator emission.

Thus, increase of the doping thallium impurity concentration in the initial solution causes habitus changes in the growing KDP crystals. An anisotropy of thallium impurity incorporation into the prism and pyramid growth sectors of ADP crystals is revealed which may be caused by the charge state of the growth planes {100} and {101}. Incorporation of thallium impurity into KDP crystals is limited by the difference in ionic radii of K^+ and Tl^+ cations. The structure perfection of thallium-doped KDP and ADP crystals becomes not deteriorated as the thallium concentration increases up to 1.0 mass %.

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Вирощування легованих талієм кристалів KDP та ADP: структурні та оптичні параметри

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Вивчено вплив активатора талію на кінетику росту та структурну досконалість кристалів KDP та ADP, характер входження і розподілу його у кристалічній гратці та на фотолюмінесційні властивості. Виявлено анізотропію входження домішки талію у сектори росту призми та піраміди кристалів ADP, що може бути обумовлено зарядовим станом площин росту {100} і {101}. У кристалах KDP входження домішки талію лімітується відмінністю йонних радіусів катіонів K^+ і Tl^+. При легуванні талієм до 1,0 мас.% кристалів KDP і ADP змінення структурної досконалості не встановлено. При цьому виявлено збільшення параметра гратки a на $0{,}9\cdot10^{-3}\pm3\cdot10^{-5}$ Å та зменшення параметра c на $1{,}1\cdot10^{-3}\pm3\cdot10^{-5}$ Å для ADP кристалів. Смуга поглинання талію у кристалах KDP:Tl^+ та ADP:Tl^+ знаходиться у межах 220 нм, а максимум смуги емісії знаходиться на довжині хвилі 280 нм.